Peer Review File

Manuscript Title: Earth Shaped by Primordial H2 Atmospheres

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1:

Motivated by exoplanets with atmospheres such as sub-Neptunes, this paper models the interaction between hydrogen-rich primordial atmospheres and the interiors of the planetary embryos that built Earth. The authors show that these interactions can explain the density deficit in Earth's iron core and an oxidation state similar to the observed one, and also produce water.

Overall, I think this model is pretty interesting, but I feel like it's not fully developed enough to feel really compelling. My takeaway is that this paper says: if Earth's constituent embryos grew to 0.2 Earth masses or more during the gas disk phase and had thick H2 primordial atmospheres, then interactions between those atmospheres and the magma ocean would explain the density deficit in Earth's core, and produce water as a byproduct.

There are two significant issues that confuse me about this paper.

The first is how well this model actually matches constraints related to Earth's water, namely the amount of water and its isotopic signature (D/H ratio). My first impression was that the paper claimed to explain the origin of all of Earth's water by this mechanism (as in Ikoma & Genda 2006). However, in the Supplementary Information, it is mentioned offhand that "Our model D/H values thus allow for non-solar sources of hydrogen comprising roughly half to 2/3 of the mass of Earth's hydrogen, excluding unconstrained sources of isotope fractionation."

The evolution of the D/H in different reservoirs is discussed in that same paragraph in the Supplementary text, but that discussion is very hard to follow. I expect, from calculations by Genda & Ikoma (2008), that the D/H ratio should evolve in time as the hydrogen atmosphere is lost to space, but that process does not seem to be modeled in the present paper. This brings up some big questions, such as:
- What does the atmospheric and D/H evolution look like in the authors' model? Is it consistent with the present-day D/H of the oceans and bulk Earth?
- How does the D/H evolution correlate/interconnect with the evolution of Earth's oxidation state and core density deficit? This should be a dynamic system in terms of heating/cooling as well as atmospheric accretion/loss, not to mention collisions.
- Is the present model consistent with the origin and evolution of noble gases (Ne, Kr, Xe in particular) in Earth's atmosphere and interior?

The D/H ratio isn't just a little detail, it's the main way of constraining the origin of Earth's water (which used. I'll note that Ikoma and Genda's model has been criticized not in the details, but rather in terms of the overall context. For instance, Earth's Nitrogen isotope ratios are a good match to

carbonaceous chondrites (as is Earth's water's D/H). On the subject of an in-gassing origin of water, Meech & Raymond (2020) wrote: "It remains to be seen whether nebular gas can explain the origin of the bulk of Earth's water. This mechanism clearly requires Earth to have accreted and later lost a thick hydrogen envelope. While such a process is a likely outcome of growth within the gaseous disk, it seems a cosmic coincidence for the parameters to have been right for Earth to end up with the same D/H ratio (and 15N/14N ratio) as carbonaceous chondrites (Marty 2012)."

My second issue is the planet formation context, which is not spelled out in the paper.

If we accept the key assumption that Earth's embryos were more than 0.2 Earth masses, what would this imply for planet formation? One obvious consequence is gas-driven migration. This is not a big surprise, as migration has been included in simulations of terrestrial planet formation as far back as Morishima et al (2008, and likely earlier). Mars-mass embryos are at the limit of significant migration, so 0.2-0.5 Earth-mass embryos would certainly undergo significant migration. Either these embryos would have originated farther from the Sun and migrated inward (as in, e.g., Johansen et al 2021), or perhaps been formed in a zone of convergent migration around Earth's orbit (Lyra et al 2010, Broz et al 2021).

Another piece of the puzzle comes from the meteorite isotopic dichotomy (Warren 2011, Kruijer et al 2017, many others). Earth is somewhat off of the non-carbonaceous line, such that Earth does appear to have accreted a fraction of carbonaceous material. Fig 5C from Burkhardt et al (2021) shows that the most likely contribution of carbonaceous material is a few percent, which is consistent with dynamical models that deliver water such as the Grand Tack (see O'Brien et al 2014) or just scattering during the gas giants' growth (Raymond & Izidoro 2017).
But a few percent of carbonaceous chondrite material would easily provide all of Earth's water and match Earth's D/H and Nitrogen isotopes (e.g. Marty 2012). Does this mean that, for the present model to really be the origin of Earth's water, little to no carbonaceous material can have contributed to Earth's growth? That naively seems permissible according to Fig 5C of Burkhardt et al, but would also have big implications for Solar System formation. (Note that the pebble accretion model of Johansen et al 2021 invokes a much larger fraction of Earth's mass originating in carbonaceous material).

It's also worth comparing the implications of a relatively well-accepted model that has been developed over the past 20 years involves Earth growing primarily from Enstatite chondrite-like building blocks with a small contribution (a few percent) from carbonaceous chondrite-like material (e.g., Morbidelli et al 2000, Burkhardt et al 2021). That model also roughly explains Earth's oxidation state (e.g. Rubie et al 2016) and is explicitly coupled to models for the dynamical evolution of the early Solar System, unlike the present model. Would such a model be compatible with the present one? How would adding the effect of early H2 atmospheres change this picture?

These are open-ended questions designed to guide how to put this new scenario in a larger context.

Overall, I feel that the idea presented here is new and interesting. However, the paper could benefit from more development, perhaps in terms of adding time evolution (such as for the evolution of the D/H ratio) and a clearer vision for how it fits in a full planet formation context.

A few detailed comments:

Fig 1 is extremely hard to interpret. As an astronomer I am lost. Where does it actually show water being produced? After reading the paper through multiple times I realized that these must all be "equilibrium" calculations in which nothing changes, correct? This feels so strange given how dynamic the planet formation process is.

How long does it take for H to be mixed into the magma ocean, produce water and affect the Earth's oxidation state and core density? Will it happen regardless, as Mars-mass embryos grow by collisions, or does a >0.2 ME embryo have to form within the gas disk? [I eventually figured this one out, but I feel like it should be spelled out more clearly.]

Ikoma and Genda (2006) found a slightly different lower limit in planet/embryo mass for a magma ocean (0.3 Earth masses in that study vs 0.2 in the present paper). What is the reason for the difference?

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Referee #2:

GENERAL COMMENTS:

The manuscript (ms) uses a thermodynamic model to examine how chemical exchange between a core, mantle and atmosphere of a planetary embryo (0.3-0.5 Earth mass) with a magma ocean, and hydrogen atmosphere might explain, 1) Earth's H2O (the ocean and water in the silicate Earth) relative to very dry starting materials in the inner solar nebula, 2) the density deficit of Earth's core relative to pure iron & nickel, which is ~10%, and (3) the relatively oxidized state of Earth's mantle compared to starting materials. The idea is that embryos evolve to have copious water, a core deficit, and more oxidized silicate mantle, then a few evolved embryos coalesce to form the Earth. The ms claims (line 19): "Reaction with hydrogen atmosphere...provides a simple explanation for fundamental [these three] features of Earth's geochemistry" and (line 261), "The result is a unified, self-consistent explanation for a number of important features of Earth related by a single overarching process of oxidation and reduction (redox) chemistry triggered by reactions between H2 and magma oceans".

Let me start with the positive, which is that the production of a few oceans' worth of water from the reaction of hydrogen with oxygen in the silicate mantle is an interesting result, and so is the prediction of the density deficit of the core due to incorporation of hydrogen. Where Earth's water came from is conventionally attributed to stochastic impacts of icy material scattered inwards from the outer asteroid belt. A caveat on the core density deficit is that the incorporation of hydrogen seems to be large compared to standard estimates in the literature [see below].

Now for the negative. Unfortunately, the claim that the redox state of the silicate mantle is due to reactions triggered by the H2 atmosphere is 100% INCORRECT. It falls foul of redox conservation – if something gets oxidized, something else must be reduced -- which is as inviolable as mass or energy

conservation. Put simply, H2, as the strongest reducing agent, cannot oxidize the silicate Earth (mantle). H2 can only react with the silicate Earth and reduce it. To be more specific, H2O made from H2 reacting with silicate O will chemically *reduce* the mantle.
Now, from the H2O thus made, the model can extract H and put it in the Fe core, which will *oxidize* the mantle. But this shuffling around of hydrogen is clearly a zero-sum game in redox balance that does nothing to the mantle redox in net. The only process described explicitly in the ms that does oxidize the silicate Earth (e.g., see Fig. 3) is the reduction of Si from +4 oxidation number in the mantle (as SiO2) to 0 in the core (as Si), which must be balanced by equivalent oxidation of the mantle's iron:
1/2(SiO2) + Fe (from the core) —> FeO (into the mantle) + 1/2Si (to the core)
In fact, the results of the model (Fig. 1, lower left panel) show no dependence of redox state of the silicate Earth on the H2 fractional mass, as one might expect from basic redox principles expressed above. The ms is therefore incorrect and misleading in its interpretation of the model results by claiming that the H2 is responsible for oxidation of the silicate mantle, as quoted above in the summary.

In fact, the H2 atmosphere is a very small redox reservoir relative to the entire planet. Adding H2 permits generation of H2O, which is important for making water, which is a small quantity relative to the total mass of the Earth. Instead of hydrogen being the oxidizing agent (which offends my sensibilities as a geochemist as both a self-contradiction and oxymoron), equilibration of the assumed initial conditions is presumably causing the "self-oxidation" of the mantle by loss of reductant to the core. An appropriate discussion of redox balance is absent from the ms. Is loss of Si to the core accounting for the redox balance, given that this is the only process that is highlighted and makes sense? In Table S3, the unequilibrated state has fO2 of IW-5.8, which is equilibrated to fO2 of IW-2. Presumably, if the model started with the same initial conditions as Table S3 but with no atmospheric H2, and equilibration was run, then it would also end up with IW-2. No such control run is presented – proving the lack of a role for H2 -- although Fig. 1 (lower left panel) is suggestive of this result.

The ms needs to be revised substantially to remove the misleading interpretation about H2 causing oxidation of the silicate mantle. For example, the overview figure, Fig. 2, has a caption that says, "The model for equilibration between magma oceans and H2-rich atmospheres (vertical black line) results in an increase in oxygen fugacity from values similar to Mercury and E chondrites, representing the inner solar system, to the value for Earth". In fact, the H2 is *NOT* increasing the oxygen fugacity because it can't because H2 is a reducing agent.

Let me now turn to a query on the production of water. The ms states (lines 152-154) that "Water produced in the interiors of the embryos and in the atmosphere partitions according to the solubility of water in the magma ocean" so water solubility is of critical importance. But this approximation has large uncertainties as the treatment derived from Schlichting and Young (2018) relies heavily on the experimental work of Hirschmann+ (2012), which demonstrated that H2 solubility (not H2O solubility) is likely heavily influenced by silicate composition, and extrapolation to higher pressures outside that study (> 4 GPa) is unverified. Is it possible that both H2 and H2O dissolve in the silicate at these fO2 values or is it expected to be only H2? If H2O is dominant, then maybe the lack of data on H2 is less of an issue. The speciation treatment and caveats on extension to high pressure are

unclear in the present ms.

Finally, a query on the core deficit. The ms says (lines 155-168), “For the 10 % density deficit in embryo metal obtained from a body composed of 0.3% by mass H, the calculated metal cores are composed of 94.6 % by mass Fe, 3.8 % Si, 0.9 % O, and 0.7 % H.” A recent review (Hirose+ 2021. Light elements in the Earth’s core. Nat Rev Earth Environ 2, 645–658 https://doi.org/10.1038/s43017-021-00203-6) gives the likely range of compositions for the outer (Fe + 5% Ni + 1.7% S + 0–4.0% Si + 0.8–5.3% O + 0.2% C + 0–0.26% H by weight) and inner core (Fe + 5% Ni + 0–1.1% S + 0–2.3% Si + 0–0.1% O + 0–1.3% C + 0–0.23% H by weight). At face value, the estimate from the model in the ms for H in the core is too high by a factor of ~3 compared to currently accepted values. In lines 250-258, the ms says, “Omission of Ni is not expected to have a significant effect” but perhaps it does, as does the neglect of carbon and nitrogen?

One final point is that the discussion of isotopes in the supplementary material is almost like a separate paper. Isotopes are not really discussed in the main text. The dichotomy is unusual.

Overall, I think the paper presents an intriguing hypothesis for where the water of the Earth came from and the origin of the core density deficit in the context of early rocky planets having H2 envelopes, but the paper needs revision on the issue of redox. The current version of the ms is unacceptable because of the lack of a discussion of redox balance that correctly explains how the silicate mantle is oxidized in the model. I consider this point rather fundamental. But it could be remedied.

SPECIFIC COMMENTS:

- Line 17: “Oxidation ensues...as Si, along with H and O, allows with Fe in the cores”. Loss of O will reduce the silicate mantle, so this abstract sentence is misleading. Also, the H entering the core is coming from H2O, which came from O in the silicate mantle, and so is having neither an oxidizing nor reducing effect on the silicate mantle in net, as explained in general comments.
- Line 21: the word “fictive” is better replaced by the less pretentious word “possible”
-Line 47: the radius gap was first reported in Fulton et al. and it seems appropriate to cite the discovery paper (Fulton BJ, Petigura EA, Howard AW, et al. (2017) The California-Kepler Survey. III. A Gap in the Radius Distribution of Small Planets. Astron J 154, doi:ARTN 109 10.3847/1538-3881/aa80eb).
- line 49: “hydrogen-rich envelopes that were lost over time” is better expressed as “...lost early”. This is happening in the first ~100 m.y., not the rest of 4.5 Gyr geologic history.
- Line 64: tau is optical depth of what wavelength range? It should say “optical depth in thermal infrared”, I believe.
- Line 69, “If exchange is sufficiently efficacious...” The phrase is lacking a noun or appropriate adjective: Exchange of what? A better phrase would presumably say, “If chemical exchange is efficient...” – also replacing efficacious with a less pretentious word.
- Line 74: This almost looks like 100^19 rather than 100 because of the citation, which is confusing. Move the citation to the end of line 76, perhaps.
- Line 123: "We fixed the initial concentration...". Suggest replacing with "We assume an initial concentration..." or similar.

- Line 125. “reduced nature...of E chondrites and Mercury” It would be nice to specify the oxidation state here up front in terms of fO2 of these bodies and give bulk silicate Earth, i.e., where we need to get to.

Figure 1: This figure is poorly labeled in many ways, making it confusing for a reader to follow and hard for a reviewer even to refer to The panels should be conventionally labeled as a (upper left), b (upper right), c (lower left), and d (lower right), so that the reader knows which one is being discussed in the text. The text refers only to Fig. 1 when only one panel is being discussed in a specific paragraph. Some other labels would help the reader. Where is 1 ocean’s worth of water on Fig 1b in terms of surface pressure of steam, say? Where is Bulk Silicate Earth oxygen fugacity on Fig. 1a? Yes, it’s buried in the text somewhere later, but that’s not the point, which is to make it easy for the reader. The vertical axis of Fig. 1b should be labeled “H2O weight % of body”, I believe, to help the reader. Why is “Earth’s embryos this study” at 0.2 mass fraction of hydrogen in Fig. 1a, c and b, but 0.002% on Fig. 1c? The caption needs to say. Labeling is also uneven: Fig. 1a: Change the x-axis to be mass fraction of H2 in %, to match other panels.

Figure 2: The vertical black line is the model with the "fiducial" parameters described in the text? Consider labeling this black line "Fiducial Model".

- Figure 3:
- Isn’t it physically unlikely that the Stage 1 planet does not have an atmosphere as indicated by “No atmosphere”? There will presumably be some impact degassing even if the atmosphere is continuously escaping and/or some rock vapor.
- Consider distinguishing the Stage 2 and Stage 3 atmospheres with different colors. Stage 2 should be very H2-rich, and Stage 3 should be mostly H2O steam?
- Line 144: "Our results are not sensitive to this uncertainty.". Be more specific about what uncertainty: “this uncertainty in pressure”. Right?

- Line 202: What about other mechanisms in the literature that could explain the density deficit of the core, and the oxidation state of the mantle? For example, iron disproportionation during core formation has been discussed for oxidizing the silicate mantle. Why is this wrong compared to the present model? There seems a lack of context for other ideas in the literature about how the silicate mantle was oxidized or where the core deficit came from.
-Line 206-7: “arrows in Figure 1” – which arrows? There are several. Perhaps labeling the panels a-d might help here.
- Line 234: “sufficient mass to retain primary atmospheres of H2”. Retain for how long? Some mention of timescale is needed here. Earth did not retain its primary atmosphere.
--Line 257: “for exchange”. Exchange of what? Please provide clarity in the writing.

Author Rebuttals to Initial Comments:

Reviewer 1

Preface Motivated by exoplanets with atmospheres such as sub-Neptunes, this paper models the interaction between hydrogen-rich primordial atmospheres and the interiors of the planetary embryos that built Earth. The authors show that these interactions can explain the density deficit in Earth's iron core and an oxidation state similar to the observed one, and also produce water.

Overall, I think this model is pretty interesting, but I feel like it's not fully developed enough to feel really compelling. My takeaway is that this paper says: if Earth's constituent embryos grew to 0.2 Earth masses or more during the gas disk phase and had thick H2 primordial atmospheres, then interactions between those atmospheres and the magma ocean would explain the density deficit in Earth's core, and produce water as a byproduct.

Response: The summary is essentially correct.

General comment 1 The first is how well this model actually matches constraints related to Earth's water, namely the amount of water and its isotopic signature (D/H ratio). My first impression was that the paper claimed to explain the origin of all of Earth's water by this mechanism (as in Ikoma & Genda 2006). However, in the Supplementary Information, it is mentioned offhand that "Our model D/H values thus allow for non-solar sources of hydrogen comprising roughly half to 2/3 of the mass of Earth's hydrogen, excluding unconstrained sources of isotope fractionation."

The evolution of the D/H in different reservoirs is discussed in that same paragraph in the Supplementary text, but that discussion is very hard to follow. I expect, from calculations by Genda & Ikoma (2008), that the D/H ratio should evolve in time as the hydrogen atmosphere is lost to space, but that process does not seem to be modeled in the present paper. This brings up some big questions, such as: - What does the atmospheric and D/H evolution look like in the authors' model? Is it consistent with the present-day D/H of the oceans and bulk Earth? - How does the D/H evolution correlate/interconnect with the evolution of Earth's oxidation state and core density deficit? This should be a dynamic system in terms of heating/cooling as well as atmospheric accretion/loss, not to mention collisions. - Is the present model consistent with the origin and evolution of noble gases (Ne, Kr, Xe in particular) in Earth's atmosphere and interior?

The D/H ratio isn't just a little detail, it's the main way of constraining the origin of Earth's water (which used. I'll note that Ikoma and Genda's model has been criticized not in the details, but rather in terms of the overall context. For instance, Earth's Nitrogen isotope ratios are a good match to carbonaceous chondrites (as is Earth's water's D/H). On the subject of an in-gassing origin of water, Meech & Raymond (2020) wrote: "It remains to be seen whether nebular gas can explain the origin of the bulk of Earth's water. This mechanism clearly requires Earth to have accreted and later lost a thick hydrogen envelope. While such a process is a likely outcome of growth within the gaseous disk, it seems a cosmic coincidence for the parameters to have been right for Earth to end up with the same D/H ratio (and 15N/14N ratio) as carbonaceous chondrites (Marty 2012)."

Response 1: The reviewer rightly points out that D/H has been a principal arbiter for the origin of Earth's water, historically. Nonetheless, as a counterpoint to the quote from Meech & Raymond (2020) they cite, we point out that the high D/H ratios among cometary ices, chondrites, representing asteroids, Earth's water, and even icy moons in the Solar System, are just as likely to be due to a "convergent evolution" of a variety of process as they are the result of simple binary mixing between solar gas and a single high D/H source (e.g. , specific water

ices). This is because any process that involves transfer of hydrogen isotopes back and forth between molecular hydrogen and water results in water having the greater D/H, including ion-molecule reactions in the interstellar medium (at ca. 10 to 20 K), kinetics involving neutral molecular species (atmospheres at temperatures at or below the equilibrium temperatures of roughly 200 to 300 K), and equilibrium exchange at all temperatures, especially at room temperatures and below. Inspection of our Figure S5 in our supplement illustrates that terrestrial water and/or bulk Earth do not coincide precisely with meteoritic (asteroidal) values, and asteroidal and cometary values have large ranges.

In response to the reviewer's suggestion that we should address the implications of D/H for our model, we added section 5.2 to the supplementary text explaining how our model might be useful in understanding the high D/H of terrestrial water relative to a primordial solar gas. In the model of Genda and Ikoma mentioned by the reviewer, higher D/H in atmospheric water is balanced by slow (over billion year timescales) hydrodynamic escape of isotopically light hydrogen. Sharp and Olsen (2022, Geoch. Cosmochim. Acta) also suggested that the high D/H of Earth's water was due to hydrodynamic escape, in this case as H rather than H_2. A slow loss of hydrogen over billions of years is not part of our model. Rather, in our case, the requisite low-D/H sinks for hydrogen that balance the high D/H of terrestrial water could be the metal cores; hydrogen isotope equilibration between embryo metal cores, silicate mantles, and atmospheres results in a high-D/H atmospheres and low-D/H metal cores.

We show that the enhanced rates of hydrogen exchange in the upper regions of atmospheres where radicals serve as reactive intermediates are sufficient to allow for the possibility that D/H exchange between water and hydrogen in the atmosphere could have been at low temperatures (e.g., 237 K, see revised text). The result, shown in the revised Figure S5, illustrates that with this stipulation of low temperatures for D/H exchange in the atmosphere, the high D/H of terrestrial water, and that of the mantle in large part inherited from surface water, are consistent with a solar-like source of primordial hydrogen. Again, this is only possible because the counterbalance to the high D/H of the atmospheric waters is hydrogen in the liquid metal cores, with the magma oceans serving as the conveyors linking the metal cores to the atmospheres. A more thorough atmosphere model for these embryos awaits a separate work and will likely be a project unto itself.

Regarding the $^{15}N/^{14}N$ ratio of Earth relative to chondrites, the ratios for the primordial Earth and its relationship to various chondrite values are unsettled, as described, for example, by Labidi et al. (2020, Nature). Regarding noble gases, we point out in the supplement that our results are satisfactorily consistent with Ne, an element where the primordial isotope ratios ($^{20}Ne/^{22}Ne$) for Earth ($\sim$ 12.6), E chondrite ($\sim$ 10.5) and solar ($\sim$ 13.7) are sufficiently distinct as to provide purchase on the problem, unlike Ar, for exaple (Lammer et al. (2020, Icarus). Sharp and Olsen (2022) made an attempt to constrain the different noble gas systems with mixing with a solar gas. The results are not entirely satisfactory, with distinct sources for different elements, likely because of complicated degassing histories for various species over time. For this reason, and because of limited variability in some cases, we do not view Xe, Kr and Ar isotopes as robust arbiters for our model, or any other.

General comment 2 If we accept the key assumption that Earth's embryos were more than 0.2 Earth masses, what would this imply for planet formation? One obvious consequence is gas-driven migration. This is not a big surprise, as migration has been included in simulations of terrestrial planet formation as far back as Morishima et al (2008, and likely earlier). Mars-mass embryos are at the limit of significant migration, so 0.2-0.5 Earth-mass embryos would certainly undergo significant migration. Either these embryos would have originated farther from

the Sun and migrated inward (as in, e.g., Johansen et al 2021), or perhaps been formed in a zone of convergent migration around Earth's orbit (Lyra et al 2010, Broz et al 2021).

Response 2: We agree with the reviewer that gas-driven migration may have played a role during formation, and has been previously investigated in the literature. As the type-1 migration rate scales linearly with embryo mass, a 0.2 Earth-mass embryo is expected to migrate about twice as fast (and far) as a Mars-sized embryo in a smooth disk. However, as mentioned by the reviewer, our understanding of both the magnitude, direction and even the exact role of type-1 migration is still evolving as it depends on the exact disk density profile, which is likely not smooth, and probably also how the disk disperses (e.g. Liu et al 2017, who investigate outward migration in the final stages of disk dispersal). We still have trouble interpreting the architecture and general absence of mean-motion resonances in the super-Earth/sub-Neptune exoplanet population, for which type-1 migration should have played an even bigger role due to their larger masses. So for all these reasons, quantifying the exact role of gas-driven migration remains an active area of research which is not part of the current manuscript.

General comment 2 continued: Another piece of the puzzle comes from the meteorite isotopic dichotomy (Warren 2011, Kruijer et al 2017, many others). Earth is somewhat off of the non-carbonaceous line, such that Earth does appear to have accreted a fraction of carbonaceous material. Fig 5C from Burkhardt et al (2021) shows that the most likely contribution of carbonaceous material is a few percent, which is consistent with dynamical models that deliver water such as the Grand Tack (see O'Brien et al 2014) or just scattering during the gas giants' growth (Raymond & Izidoro 2017). But a few percent of carbonaceous chondrite material would easily provide all of Earth's water and match Earth's D/H and Nitrogen isotopes (e.g. Marty 2012). Does this mean that, for the present model to really be the origin of Earth's water, little to no carbonaceous material can have contributed to Earth's growth? That naively seems permissible according to Fig 5C of Burkhardt et al, but would also have big implications for Solar System formation. (Note that the pebble accretion model of Johansen et al 2021 invokes a much larger fraction of Earth's mass originating in carbonaceous material).

Response 2 continued: The conclusion of the Burkhardt et al. (2021) review, referenced by the reviewer, is that Mo, among all elements with stable isotope anomalies, is virtually unique in seeming to require a finite amount of CC contribution to Earth and Mars. For other isotope systems, Ti and Cr, for example, it is not clear that there is any CC contribution (e.g. , Figure 4 from Burkhardt et al. 2021). Figure 5c from Burkhardt et al., portraying the results of their monte carlo simulations, is actually consistent with zero CC as well (the tails of the distributions intersect the origin at a relatively high PDF value). The question of how much water was delivered from late CC material seems to still be an open question, as discussed above. In all cases, there is nothing about our model that precludes some late addition of exogenous material. In the revised text we added a short sentence at line 180 stating this fact. The point of our paper is that the basic features dealt with in our paper do not *require* delivery of exogenous material. Our hope is that our paper will generate discussion along the lines described by the reviewer.

Detailed comments with responses:

Fig 1 is extremely hard to interpret. As an astronomer I am lost. Where does it actually show water being produced? After reading the paper through multiple times I realized that these must all be "equilibrium" calculations in which nothing changes, correct? This feels so strange given how dynamic the planet formation process is.

These are indeed equilibrium calculations. At such high temperatures and long times, this is not as strange as it might seem, at least to first order. The comment suggests that Figure 1B (we added letters to the panels per the

request of Reviewer 2) required some clarification. We added a clear indication of 1 ocean's worth of water to the figure and amended the caption, as outlined below in response to Reviewer 2.

How long does it take for H to be mixed into the magma ocean, produce water and affect the Earth's oxidation state and core density? Will it happen regardless, as Mars-mass embryos grow by collisions, or does a > 0.2 ME embryo have to form within the gas disk? [I eventually figured this one out, but I feel like it should be spelled out more clearly.]

Yes, the embryos must form in the disk, and embryos must be > 0.2 ME because one must have hydrogen and the hydrogen must be able to exchange with the magma ocean. The timescales for overturn by convection in the molten mantle of the embryos is discussed in the paragraph starting at line 69 of the revised text. In the revised text at line 76 we added explicitly the turnover time for the mantles of order 10^4 yr implied by the analysis starting at line 70 (divide mantle radius by convective velocity scaled by the reduced radiative flux). It is convection that must be sufficient to allow for equilibration of the entire system. Our calculations suggest that it would be.

In response to this comment and another one similar to it, we added an additional figure to the supplmentary text, Figure S1, showing the relationship between embryo mass, surface temperature, and existence of a primary atmosphere. This should clarify the setting we describe for formation of embryos in the disk. We note that the relationship between the mass of the embryos and their interaction with the disk is a significant portion of the text as written (e.g., lines 78-98 and lines 130-149 in the revised text).

Ikoma and Genda (2006) found a slightly different lower limit in planet/embryo mass for a magma ocean (0.3 Earth masses in that study vs 0.2 in the present paper). What is the reason for the difference?

Conceptually, 0.2 Earth masses is derived by setting the thermal speed of hydrogen molecules at 1500K equal to the escape velocity of a given mass embryo. This yields that only embryos more massive than about 0.2 Earth masses have enough gravity to keep hydrogen gas at 1500K gravitationally bound. We therefore regard 0.2 Earth masses as an absolute lower limit. Ikoma and Genda (2006) used a somewhat different approach (although the fundamental physics - is of course the same) and modeled part of the accretion phase, which is why their results depend, in addition to embryo mass, on accretion/cooling luminosity and envelop/grain opacity. Other small difference can arise from the differences in the exact adiabatic index that describes the radial atmospheric profile. We find it very encouraging that these two different approaches yield so similar results.

Reviewer 2

Preface The manuscript (ms) uses a thermodynamic model to examine how chemical exchange between a core, mantle and atmosphere of a planetary embryo (0.3-0.5 Earth mass) with a magma ocean, and hydrogen atmosphere might explain, 1) Earth's H2O (the ocean and water in the silicate Earth) relative to very dry starting materials in the inner solar nebula, 2) the density deficit of Earth's core relative to pure iron nickel, which is $\sim 10\%$, and (3) the relatively oxidized state of Earth's mantle compared to starting materials. The idea is that embryos evolve to have copious water, a core deficit, and more oxidized silicate mantle, then a few evolved embryos coalesce to form the Earth. The ms claims (line 19): "Reaction with hydrogen atmosphere...provides a simple explanation for fundamental [these three] features of Earth's geochemistry" and (line 261), "The result is a unified, self-consistent explanation for a number of important features of Earth related by a single overarching process of oxidation and reduction (redox) chemistry triggered by reactions between H2 and magma oceans".

Let me start with the positive, which is that the production of a few oceans' worth of water from the reaction of hydrogen with oxygen in the silicate mantle is an interesting result, and so is the prediction of the density deficit of the core due to incorporation of hydrogen. Where Earth's water came from is conventionally attributed to stochastic impacts of icy material scatter

Response: We are pleased that the basics were clear to the reviewer, and where we were not clear, the reviewer's comments have improved the presentation, as described below.

General comment 1 Now for the negative. Unfortunately, the claim that the redox state of the silicate mantle is due to reactions triggered by the H2 atmosphere is 100% INCORRECT. It falls foul of redox conservation – if something gets oxidized, something else must be reduced – which is as inviolable as mass or energy conservation. Put simply, H2, as the strongest reducing agent, cannot oxidize the silicate Earth (mantle). H2 can only react with the silicate Earth and reduce it. To be more specific, H2O made from H2 reacting with silicate O will chemically *reduce* the mantle. Now, from the H2O thus made, the model can extract H and put it in the Fe core, which will *oxidize* the mantle. But this shuffling around of hydrogen is clearly a zero-sum game in redox balance that does nothing to the mantle redox in net. The only process described explicitly in the ms that does oxidize the silicate Earth (e.g., see Fig. 3) is the reduction of Si from +4 oxidation number in the mantle (as SiO2) to 0 in the core (as Si), which must be balanced by equivalent oxidation of the mantle's iron: 1/2(SiO2) + Fe (from the core) $\rightarrow$ FeO (into the mantle) + 1/2Si (to the core) In fact, the results of the model (Fig. 1, lower left panel) show no dependence of redox state of the silicate Earth on the H2 fractional mass, as one might expect from basic redox principles expressed above. The ms is therefore incorrect and misleading in its interpretation of the model results by claiming that the H2 is responsible for oxidation of the silicate mantle, as quoted above in the summary.

In fact, the H2 atmosphere is a very small redox reservoir relative to the entire planet. Adding H2 permits generation of H2O, which is important for making water, which is a small quantity relative to the total mass of the Earth. Instead of hydrogen being the oxidizing agent (which offends my sensibilities as a geochemist as both a self-contradiction and oxymoron), equilibration of the assumed initial conditions is presumably causing the "self-oxidation" of the mantle by loss of reductant to the core. An appropriate discussion of redox balance is absent from the ms. Is loss of Si to the core accounting for the redox balance, given that this is the only process that is highlighted and makes sense? In Table S3, the unequilibrated state has fO2 of IW-5.8, which is equilibrated to fO2 of IW-2. Presumably, if the model started with the same initial conditions as Table S3 but with no atmospheric H2, and equilibration was run, then it would also end up with IW-2. No such control run is presented – proving the lack of a role for H2 – although Fig. 1 (lower left panel) is suggestive of this result.

The ms needs to be revised substantially to remove the misleading interpretation about H2 causing oxidation of the silicate mantle. For example, the overview figure, Fig. 2, has a caption that says, "The model for equilibration between magma oceans and H2-rich atmospheres (vertical black line) results in an increase in oxygen fugacity from values similar to Mercury and E chondrites, representing the inner solar system, to the value for Earth". In fact, the H2 is *NOT* increasing the oxygen fugacity because it can't because H2 is a reducing agent.

Response 1: The reviewer is entirely correct, H_2 is not the source of the increase in FeO to the mantle in our calculations, and we note at the same time that electrons are balanced by any trajectory through the reaction space defined by the 18 reactions (including redox involving hydrogen) considered, as evident by inspection. This lengthy criticism arises because of a misunderstanding, precipitated by the way our manuscript was written.

We tried to convey that the high oxygen fugacity obtained in our model is self consistent with the core density we obtain, bearing in mind that the coupled equations representing the 18 equilibria and associated mass balance constraints are solved simultaneously. We did not wish to imply that somehow hydrogen was acting as an oxidant. Rather, we wish to make clear that our model simultaneously produces the right density deficit in the core by virtue of adding H as well as Si and O to the Fe alloy (H dominates the density deficit). The increase in FeO in the mantles of the embryos is indeed the result of Si replacing Fe in the metal alloy, in just the right amount, as we explained in our original text. In response to this comment, we rewrote the section on oxygen fugacity in the main text to make it clear that the link between the f_{O_2} we derive and H in the core is in the form of self consistency rather than direct causality. To make this more clear, we point out in the revised text that if one follows the arrow in Figure 1A of the paper along the core density deficit of 8% isopleth to higher temperatures and lower H, one can preserve the metal density deficit by replacing H with more Si and O in the metal. However, the cost of this alternative interpretation is that the FeO in the mantle, displaced by Si in the metal alloy, is too high, resulting in an intrinsic oxygen fugacity that is too high relative to Earth's observed value (Figure 1C). Our point is that our model involving H simultaneously satisfies the constraint of the density deficit in the core and intrinsic oxygen fugacity recorded by FeO in the mantle, and this need not have been the outcome, as explained more explicitly in the revised text. We have endeavored to modify the text in several places to avoid further confusion on this point (in particular the paragraph that began on line 145 in the original text, and now appears at approximately line 150 in the revised text, and in the caption to Figure 1).

As an aside, the reviewer is also correct that the final thermodynamic equilibrium concentration of FeO of the rock does not depend on the initial oxygen fugacity but rather on the specified bulk composition (equilibrium is by its nature not path dependent), in the present case, that of an E-chondrite-like body. We verified this many times with just the sort of "control" mentioned by the reviewer. A demonstration of the importance of the bulk composition on the equilibrium Si and O relative concentrations in metal cores is given by Righter et al. (2020, Elements).

General comment 2 Let me now turn to a query on the production of water. The ms states (lines 152-154) that "Water produced in the interiors of the embryos and in the atmosphere partitions according to the solubility of water in the magma ocean" so water solubility is of critical importance. But this approximation has large uncertainties as the treatment derived from Schlichting and Young (2018) relies heavily on the experimental work of Hirschmann+ (2012), which demonstrated that H2 solubility (not H2O solubility) is likely heavily influenced by silicate composition, and extrapolation to higher pressures outside that study ($>$ 4 GPa) is unverified. Is it possible that both H2 and H2O dissolve in the silicate at these fO2 values or is it expected to be only H2? If H2O is dominant, then maybe the lack of data on H2 is less of an issue. The speciation treatment and caveats on extension to high pressure are unclear in the present ms.

Response 2: This comment in essence asks what effects would changes in some of the thermodynamic parameters controlling partitioning of H between phases have on our results. Schlichting and Young (2022) presented a lengthy discussion of different means of extrapolating measured H_2 solubilities to higher pressures. Fortunately, in the present work, pressures at the melt-atmosphere interface are low so that no extrapolations to high pressures are necessary. We also note that new experiments presented at the recent Goldschmidt meeting, by Brugman et al. (2022), show that hydrogen solubility in pyrolite shows a similar trend to the basalt and andesite data from the Hirschmann et al. study relied on in the present work. What is more, changes in the solubility of H_2 in the magma ocean melts would manifest as changes in the mass of the initial primordial atmosphere to arrive at essentially

identical results, and we have a large range in the mass of the atmosphere permissible based on models cited in the text.

Beyond hydrogen solubility itself, the reviewer's comments raise the general point that there are uncertainties associated with the thermdoymaic data controlling the partitioning of hydrogen in all its forms between the reservoirs. In response to this general observation implied by the comment, we added section 3 to the supplementary text. In that section we present recalculations of our model in which we consider hints of non-ideal mixing between silicate and water, between silicate and H_2, and between H and its metal alloy host. The results of including all three non-ideal activity-composition relationships simultaneously are given in new Table S4 which can be compared directly with Table S1. We point out that the only tangible effect is to alter the final equilibrium pressure of the water-rich atmosphere at the magma ocean-atmosphere interface, and that the more massive atmosphere doubles the amount of water produced in our calculations with no important change in the density deficit of the core. Our model is not critically sensitive to the non-ideal mixing of H_2O, H_2, and H in their respective host phases.

We also investigate the sensitivity of our results to potential unknown uncertainties in the free energy for the reaction that partitions H between the metal alloy and silicate. We show that multiplying this free energy by factors of 1.5 and 0.5 has only negligible effects on the results, and we provide an explanation as to why this is so in the last paragraph of section 3 of the revised supplement.

General comment 3 Finally, a query on the core deficit. The ms says (lines 155-168), "For the 10 % density deficit in embryo metal obtained from a body composed of 0.3% by mass H, the calculated metal cores are composed of 94.6 % by mass Fe, 3.8% Si, 0.9 % O, and 0.7 % H." A recent review (Hirose+2021. Light elements in the Earth's core. Nat Rev Earth Environ 2, 645–658 https://doi.org/10.1038/s43017-021-00203-6) gives the likely range of compositions for the outer (Fe+5% Ni+1.7% S+0-4.0% Si+0.8-5.3% O+0.2% C+0-0.26% H by weight) and inner core (Fe+5% Ni+0-1.1% S+0-2.3% Si+0-0.1% O+0-1.3% C+0-0.23% H by weight). At face value, the estimate from the model in the ms for H in the core is too high by a factor of $\sim$3 compared to currently accepted values. In lines 250-258, the ms says, "Omission of Ni is not expected to have a significant effect" but perhaps it does, as does the neglect of carbon and nitrogen?

Response 3: Our results are not in conflict with the review by Hirose et al., as explained here. The review by Hirose et al. uses published experimental results on Fe-rich metal alloys with light elements at relevant pressures and temperatures, together with some geochemical and cosmochemical arguments, to suggest likely ranges in the concentrations of the various candidate light elments in Earth's core (outer core mainly). Hard constraints come from the experiments and consideration of seismic velocities in the core. According to Hirose et al., these hard constraints include that O in the outer core should be $<$ 3.8% or 5.3% by weight, depending on the equations of state used, that the combination of Si and O should be $<$ about 7% by weight in the present-day outer core (assuming a temperature at the CMB of 4500 K, their Figure 5c), and that H alloyed with Fe+Ni should not exceed a maximum of about 0.85% by weight if it was the dominant light element in the core. The latter is based on the constraints imposed by the core density and seismic velocities, as described by Umemoto and Hirose (2015, GRL). Our proposed core composition does not violate any of these proposed hard constraints.

The specific ranges of light elements proposed by Hirose et al. , and cited by the reviewer, are based on additional geochemical and cosmochemical inferences. Most relevant to our work is the limit of 0.26% H, which is

considerably lower than allowed by experiments and by compressional seismic velocities. This maximum value for H in the outer core comes from estimating how much total "water", or H, Earth might contain, not from experiments or seismology, but rather from their assumption that all of the water was delivered to Earth by small bodies, and so is exogenous. However, they offer the important caveat that, quoting from their paper, "It is also possible that a major source of hydrogen was the H-rich protosolar gas, a hypothesis supported by the low D/H ratio of water in the deep mantle." We agree, and this is the focus of our paper. All told, we think it is fair to say there are no real "currently accepted values" for concentrations of light elements in the core. As our proposed core composition does not violate any hard constraints based on experiments or the seismology of the core, we do not view our work as being in conflict with the review by Hirose et al. .

We should point out that the reviewer is not citing our fiducial model (our best fit), but rather the model with more H than required for the target 8% density deficit of embryo cores. We propose that the embryos had 0.5% by weight H in their metal cores, and that as a result of assembling Earth from these embryos, compression from about 40 GPa to the core-mantle boundary of the Earth at 136 GPa, the 8% density deficit becomes a 10% density deficit due to the equation of state for iron-hydride, as descrbied in our paper. The 0.7% by weight H cited by the reviewer would be the case where the embryos had a 10% density deficit, ignoring the effects of subsequent compression.

Regarding omission of C and N, their effects on alloy densities are similar to those of O and Si, as is the effect of S (Li and Fei, 2014, Treatise on Geochemistry 2nd ed.), for example. Small amounts of these elements would therefore not change the overall conclusions regarding H in the core. Other studies (e.g., Bajgain et al., 2021, Communications Earth & Environment) have concluded that liquid iron alloyed with significant carbon of up to 2 wt% can satisfy the compressional wave velocities and densities of the outer core. The argument is made that carbon is a good candidate for an important light element in the core because of its cosmic abundance. However, there is no additional evidence to favor C over any other element. Here we argue H is perhaps a superior choice not only because it is exceptionally abundant, but because we have evidence in the form of extrasolar planet evolution that H-rich atmospheres play a key role in planet formation in general. Indeed, there is evidence for a solar-like hydrogen-rich gas component in Earth from Ne isotopes.

Detailed comments with responses:

- Line 17: "Oxidation ensues...as Si, along with H and O, allows with Fe in the cores". Loss of O will reduce the silicate mantle, so this abstract sentence is misleading. Also, the H entering the core is coming from H2O, which came from O in the silicate mantle, and so is having neither an oxidizing nor reducing effect on the silicate mantle in net, as explained in general comments.

We understand why the reviewer is objecting to this sentence, and we addressed this in our revised text. However, as written, the sentence in the abstract is accurate, Si replacing Fe in the core results in addition of FeO to the mantle, and this happens together with (although not necessarily because of) addition of O and H as controlled by chemical thermodynamic equilibrium. The commonly applied measure of oxygen fugacity in planetary science is the concentration of "FeO" in the rocks (or more precisely the ratio of the mole fractions of FeO and Fe in silicate and metal, respectively), and this goes up during the process we describe. Overall, electrons are moving between silicate and metal species with the net effect of increasing $x_{\mathrm{FeO}}/x_{\mathrm{Fe}}$, resulting in higher calculated oxygen fugacities expressed as ΔIW.

- Line 21: the word “fictive” is better replaced by the less pretentious word “possible”

Done

-Line 47: the radius gap was first reported in Fulton et al. and it seems appropriate to cite the discovery paper (Fulton BJ, Petigura EA, Howard AW, et al. (2017) The California-Kepler Survey. III. A Gap in the Radius Distribution of Small Planets. Astron J 154, doi:ARTN 109 10.3847/1538-3881/aa80eb).

Agreed, we added this reference.

- line 49: “hydrogen-rich envelopes that were lost over time” is better expressed as “...lost early”. This is happening in the first 100 m.y., not the rest of 4.5 Gyr geologic history.

Actually, for super-Earths and sub-Neptune exoplanets (which are discussed line 49), hydrogen loss has been observed to occur over 100Myr to Gyr timescales (Berger et al. 2020, David et al 2021). We added the timescale range to the manuscript.

- Line 64: tau is optical depth of what wavelength range? It should say “optical depth in thermal infrared”, I believe.

It is the Rosseland mean opacity based on calculations and tables derived for exoplanets and ultracool dwarfs (e.g. Freedman et al. 2008).

- Line 69, “If exchange is sufficiently efficacious...” The phrase is lacking a noun or appropriate adjective: Exchange of what? A better phrase would presumably say, “If chemical exchange is efficient...” – also replacing efficacious with a less pretentious word.

The reviewer rightly caught us using of a bit of geochemistry jargon. We meant exchange of material and its chemical constituents. We added the descriptor ”material and chemical” in front of ”exchange” to clarify and replaced efficaceous with efficient.

- Line 74: This almost looks like 100^{19} rather than 100 because of the citation, which is confusing. Move the citation to the end of line 76, perhaps.

Because we already cited this reference in the previous sentence, we removed it from this sentence to avoid the confusion noted by the reviewer.

- Line 123: ”We fixed the initial concentration...”. Suggest replacing with ”We assume an initial concentration...” or similar.

Done

- Line 125. “reduced nature...of E chondrites and Mercury” It would be nice to specify the oxidation state here up front in terms of fO2 of these bodies and give bulk silicate Earth, i.e., where we need to get to.

Done

Figure 1: This figure is poorly labeled in many ways, making it confusing for a reader to follow and hard for a reviewer even to refer to The panels should be conventionally labeled as a (upper left), b (upper right), c (lower

left), and d (lower right), so that the reader knows which one is being discussed in the text. The text refers only to Fig. 1 when only one panel is being discussed in a specific paragraph. Some other labels would help the reader. Where is 1 ocean's worth of water on Fig 1b in terms of surface pressure of steam, say? Where is Bulk Silicate Earth oxygen fugacity on Fig. 1a? Yes, it's buried in the text somewhere later, but that's not the point, which is to make it easy for the reader. The vertical axis of Fig. 1b should be labeled "H2O weight % of body", I believe, to help the reader. Why is "Earth's embryos this study" at 0.2 mass fraction of hydrogen in Fig. 1a, c and b, but 0.002% on Fig. 1c? The caption needs to say. Labeling is also uneven: Fig. 1a: Change the x-axis to be mass fraction of H2 in %, to match other panels.

These are excellent suggestions. We changed Figure 1 accordingly and added references to Figure 1A, Figure 1C, etc. throughout the revised text.

Figure 2: The vertical black line is the model with the "fiducial" parameters described in the text? Consider labeling this black line "Fiducial Model".

The horizontal lines in panels A, C, and D are also the fiducial model with regard to temperature. Their interseciton is shown by the Earth symbol, which we think makes it clear that this is the favored model that reproduces Earth. Nonetheless, in response to this comment, we rewrote the caption to Figure 1 to clarify the meaning of the symbols. Although the caption is now fairly long, we think we have eliminated possible confusion surrounding the lines and symbols.

- Figure 3: - Isn't it physically unlikely that the Stage 1 planet does not have an atmosphere as indicated by "No atmosphere"? There will presumably be some impact degassing even if the atmosphere is continuously escaping and/or some rock vapor. - Consider distinguishing the Stage 2 and Stage 3 atmospheres with different colors. Stage 2 should be very H2-rich, and Stage 3 should be mostly H2O steam?

We considered this suggestion seriously, and could return to it. However, at present our opinion is that the use of multiple colors or symbols for multiple types of atmospheres would make the figure less accessible for those seeking to understand the salient features of our results. For example, the rock-vapor atmosphere would not be the primary atmosphere that we are describing throughout the text, and would be many orders of magnitude less massive (surface pressures of order 10^{-4} bar for rock vapor at equilibrium compared with $\sim 10^3$ bar for the H_2-rich atmosphere prior to equilibration). The two are so markedly different that it would be confusing to show them both with the only difference showing up as a change in color. Similarly, while a different color could be used for the pre-equilibration and post-equilibration atmospheres in stages 2 and 3, respectively, we instead just label stage 2 as simply "H_2" and stage 3 with a number of relevant species. The distinction should be clear from the labeling.

- Line 144: "Our results are not sensitive to this uncertainty.". Be more specific about what uncertainty: "this uncertainty in pressure". Right?

Correct. We added "in pressure" to the end of this sentence.

- Line 202: What about other mechanisms in the literature that could explain the density deficit of the core, and the oxidation state of the mantle? For example, iron disproportionation during core formation has been discussed for oxidizing the silicate mantle. Why is this wrong compared to the present model? There seems a lack of context for other ideas in the literature about how the silicate mantle was oxidized or where the core deficit came

from.

There is nothing inherently wrong with these other models. However, in the past, they were used to explain core density and oxygen fugacity as separate models. We think an attractive feature of our work is that we can explain these characteristics of Earth by a single process known to occur, using a single mathematical portrayal of the process. This model is well motivated by the importance of hydrogen in the evolution of rocky exoplanets, as described in the first portion of the text. Our paper is not meant to be a comprehensive review of the large literature on various facets of the formation of Earth, so no practical change to the present paper was made in response to this comment.

Regarding disproportionation of Fe^{2+} to Fe^{3+} and Fe^{0}, it surely had a role to play in altering the oxidation state of Earth's mantle to the values seen today, at least locally (Frost et al. 2004, Nature, Wood et al. 2006, Nature, Sinmyo et al. 2019). It may be more important for altering the mantle subsequent to initial partitioning of Fe and Si between metal and silicate during core formation. As described by Doyle et al. (2019, Science) the mole fraction of "FeO" (as total iron in silicate and oxide mantles) is a record of the intrinsic oxygen fugacity during core formation. The signature persists even after subsequent changes in iron valence state, for example. We are suggesting that based on our calculations, and those of others who have investigated the thermodynamics of Si distribution between metal and silicate, the reaction we consider here is unavoidable where silicate and Fe metal alloys approach chemical equilibrium. What is more, we show that this process of Si displacing Fe in the metal is predicted to occur in precisely the right measure as to explain the transition from E-chondrite to Earth-like oxygen fugacities in the rocky phases of Earth's progenitors.

-Line 206-7: "arrows in Figure 1" – which arrows? There are several. Perhaps labeling the panels a-d might help here. We amended Figure 1 to include labels for each panel, and now can refer to the single arrows in panels A, C, and D, and the several parallel arrows in panel B. This should improve the clarity.

- Line 234: "sufficient mass to retain primary atmospheres of H2". Retain for how long? Some mention of timescale is needed here. Earth did not retain its primary atmosphere.

At issue here is not timescales of retention of an atmosphere, but rather coexistence of primary atmospheres and magma oceans at *any* time. In order to underscore this point, we added a figure in the supplementary text, Figure S1, showing the criteria for coexistence of a primary atmosphere and a magma ocean.

-Line 257: "for exchange". Exchange of what? Please provide clarity in the writing.

We replaced "exchange" with "approach equilibrium" at what is now line 262.

Reviewer Reports on the First Revision:

Referee #1:

I appreciate the authors addressing my previous comments and making several key clarifications, especially in section 5.2 of the supplement.

The authors still do not emphasize the connection between their current model and the requirements it would place on planet formation. I don't think this needs to be done in a way that assumes any kind of final answer. To make the point: the authors model essentially unavoidably implies that orbital migration be an essential process in terrestrial planet formation. This does not mean that the authors should pretend to know exactly how that would have played out, or even what direction the embryos will migrate (because it's complicated!). But I feel that this type of chain of logic should be spelled out in the main paper, so that the reader can understand some of the broader implications of the model.

Apart from that, I don't see any other issues preventing publication. Congratulations to the authors on an interesting new model!

****

Referee #2:

Re-review of Young+ 2022

I thank the authors for their conscientious and largely comprehensive attention to the previous review comments.

I still have some easily addressed outstanding comments to improve the manuscript (ms), as follows:

1) A prior general comment was that the first version of the ms had wording that misled the reader into thinking that that the hydrogen atmosphere was somehow essential for attaining the oxidation state of the mantle. The response agrees that hydrogen (a strong reducing agent) cannot be responsible for mantle oxidation and that the cause is Si entering the Fe core from what was SiO2 above the core. I still think some vestiges of the previous misleading write-up are present. Hence:

Line 19: The sentence: "Reaction with hydrogen atmospheres thus provides a simple explanation for fundamental features of Earth's geochemist that is consistent with rocky planet formation across the galaxy" is misleading and needs to be changed to:
"Reaction with hydrogen atmospheres and metal-silicate equilibrium thus provide an explanation for fundamental features of Earth's geochemist thatis consistent with rocky planet formation across the galaxy."

If the abstract needs to cut some words to satisfy word count, the words "of our planet" on line 7 are superfluous and can be cut.

(And by the way, it was not just me: I gave an original version of the ms to a postdoc and a grad student to read. Both interpreted the initial ms as requiring a hydrogen atmosphere to get all of the chemical results, including the mantle redox, because of statements that created an impression. So, this empirical test shows that, on this point, it's not the fault of a reviewer being obtuse but rather the fault of a poorly written ms. Hence, it's critical that the ms is written in a way that avoids being misunderstood, including the abstract above).

2) Line 65: The authors response says that the optical depth on this line is the Rosseland mean, i.e., a particular weighted integral across all wavelengths suitable for an optically thick situation (unlike a Planck mean). But they didn't change the ms. The ms should be changed for accuracy, as follows, given that there are different types of optical depth:
Line 65: "τ is optical depth at the R_RCB" should be "τ is the Rosseland mean optical depth at the R_RCB".

3) Lines 153-154. I find the following sentence a bit misleading, along the lines of point #1:
"Here we find that the production of water by the coupled equilibria in our model is linked to incorporation of hydrogen into the metal phase".
This makes it sound like water is somehow derived from incorporation of hydrogen into the metal phase. It is not. So, please change to:
"Here we find that the conditions for production of water by the coupled equilibria are accompanied by incorporation of hydrogen into the metal phase."

4) Line 155: The next sentence is poorly phrased because it makes it sound like "total water" is in the metal cores.
Change "Total water and light elements in the metal cores..."
to
"Light elements in the metal cores and total water..."

5) Figure 3. I still find Figure 3 to have a few weird aspects. Apart from the suggestion of coloring the chemically different atmospheres different colors (which the authors resisted), why does the metal in "Stage 2" look like it's in a shell (colored yellow) around a silicate core and below a silicate mantle? Surely the metal would be more mixed than a shell? If not, please explain in the caption why it's drawn this way.

6) Line 248:
Suggest change "...derived from beyond 2 AU where the more oxidized carbonaceous chondrites could serve as sources"
To
"...derived from beyond 2 AU where water-rich carbonaceous chondrites could serve as sources"

Isn't the point here that the chondrites from the outer asteroid belt have more ice, i.e, are water-rich, rather than oxidized per se? On Mars, oxidation of its mantle may be partly attributable to hydrogen escape from accreted water that reacted with FeO and left oxygen behind as Fe2O3 – an old but reasonable idea explored in papers by Dreibus and Wanke. We now know (virtually for sure) that early Mars had an episode of hydrodynamic hydrogen escape (probably for ~10^8 year

timescales) because this escape is encoded in fractionation of atmospheric xenon isotopes found in Mars meteorites that is attributable to xenon ions being dragged out to space by escaping hydrogen (Cassata et al. 2022 Xenon isotope constraints on ancient Martian atmospheric escape, EPSL, https://www.sciencedirect.com/science/article/abs/pii/S0012821X21006051)

7) Line 418: Typo of “masss”

8) Supplemental:
Section 5.2: Typo of “samlll” instead of small
Also: “have delta-D greater than 0” is incorrect because chondrite meteorites sometimes have 0 as a mean value, as shown in Fig. S5. Suggest change to “have delta-D similar to or greater than 0” for accuracy.

Author Rebuttals to First Revision:

Reviewer 1

Preface I appreciate the authors addressing my previous comments and making several key clarifications, especially in section 5.2 of the supplement.

The authors still do not emphasize the connection between their current model and the requirements it would place on planet formation. I don't think this needs to be done in a way that assumes any kind of final answer. To make the point: the authors model essentially unavoidably implies that orbital migration be an essential process in terrestrial planet formation. This does not mean that the authors should pretend to know exactly how that would have played out, or even what direction the embryos will migrate (because it's complicated!). But I feel that this type of chain of logic should be spelled out in the main paper, so that the reader can understand some of the broader implications of the model.

Apart from that, I don't see any other issues preventing publication. Congratulations to the authors on an interesting new model!

Response: In response to this comment, we amended the sentence at line 93 of the revised text to read:"Surface densities greater than that of the MMSN, radial drift of disk material (Schlichting et al. 2014), radial migration of embryos themselves, and/or rapid growth facilitated by pebble accretion (Johansen et al. 2021), would have resulted in growth of embryos to several tenths of Earth masses." The change is the addition of the possibility for orbital migration of embryos and not just radial drift of disk material. The essential issue is to enumerate the many reasons that embryos might grow beyond the classical isolation mass. We appreciate the comment regarding implications for planet formation in general. However, we don't think that a fuller discussion of this broad issue will add to the point of our paper.

Reviewer 2

Line 19: The sentence: "Reaction with hydrogen atmospheres thus provides a simple explanation for fundamental features of Earth's geochemist that is consistent with rocky planet formation across the galaxy" is misleading and needs to be changed to: "Reaction with hydrogen atmospheres and metal-silicate equilibrium thus provide an explanation for fundamental features of Earth's geochemist thatis consistent with rocky planet formation across the galaxy."

Response: Done.

Line 65: The authors response says that the optical depth on this line is the Rosseland mean, i.e., a particular weighted integral across all wavelengths suitable for an optically thick situation (unlike a Planck mean). But they didn't change the ms. The ms should be changed for accuracy, as follows, given that there are different types of optical depth: Line 65: "τ is optical depth at the R_{RCB}" should be "τ is the Rosseland mean optical depth at the R_{RCB}".

Response: Done.

Lines 153-154: I find the following sentence a bit misleading, along the lines of point 1: "Here we find that the production of water by the coupled equilibria in our model is linked to incorporation of hydrogen into the metal phase". This makes it sound like water is somehow derived from incorporation of hydrogen into the metal phase.

It is not. So, please change to: “Here we find that the conditions for production of water by the coupled equilibria are accompanied by incorporation of hydrogen into the metal phase.”

Response: Done.

Line 155: The next sentence is poorly phrased because it makes it sound like total water is in the metal cores. Change “Total water and light elements in the metal cores...” to “Light elements in the metal cores and total water...”

Response: Done.

Figure 3: I still find Figure 3 to have a few weird aspects. Apart from the suggestion of coloring the chemically different atmospheres different colors (which the authors resisted), why does the metal in “Stage 2” look like it’s in a shell (colored yellow) around a silicate core and below a silicate mantle? Surely the metal would be more mixed than a shell? If not, please explain in the caption why it’s drawn this way.

Response: The figure was drawn this way to convey the possibility for metal-silicate equilibration at lower pressures than those at the core-mantle boundaries. In some prior work silicate-metal equilibration is suggested to occur at a particular depth horizon. The alternative would be to show randomly distributed blobs of iron metal.

In response to this comment, we added the following text to the caption for Figure 3 under the description of stage 2: ”Metal-silicate differentiation may have already begun at this stage.” This should provide some context for the illustration of nascent metal-silicate segregation. Given the instruction to not add many new words, we chose not to add a more detailed description of this geometry to the figure caption. Those readers interested in core formation will likely understand the significance, and for those readers who are not, this placement of the metal prior to completion of core formation will not be of any consequence to their understanding of the paper.

Line 248: Suggest change “...derived from beyond 2 AU where the more oxidized carbonaceous chondrites could serve as sources” To “...derived from beyond 2 AU where water-rich carbonaceous chondrites could serve as sources”

Response: In response to this comment, we changed the sentence to ”...derived from beyond 2 AU where the more oxidized and water-rich carbonaceous chondrites could serve as sources”. This reflects the fact that many, if not all, carbonaceous chondrite parent bodies had plentiful water, but also, they contain silicates that have larger concentrations of ”FeO” in their silicates, compared with enstatite chondrites. This applies to minerals like olivine that are not affected by aqueous alteration, so it is not only water that we are concerned with here. The point about Mars and atmospheric escape is a valid consideration, but beyond the scope of this paper. The effect of atmospheric escape could be in addition to the oxidation state of the source material for Mars under the right conditions.

Line 418: Typo of “masss”

Response: Fixed.

Supplemental: Section 5.2: Typo of “samlll” instead of small Also: “have delta-D greater than 0” is incorrect because chondrite meteorites sometimes have 0 as a mean value, as shown in Fig. S5. Suggest change to “have delta-D similar to or greater than 0” for accuracy.

Response: Fixed the typo. We revised the sentence citing δD of chondrites to "have $\delta D \geq 0$, and often much greater than zero."